

REACTIVITY OF MONOCYCLIC AROMATIC COMPOUNDS UNDER HYDROTHERMAL CONDITIONS

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INTRODUCTION

In recent years, there has been an increasing awareness among geochemists that aqueous reactions may play a significant role in the thermal maturation of organic matter in geologic environments (1,2). There are several ways in which water may enhance the reactivity of organic compounds, including serving as a solvent for reactions or participating directly as a reactant in the process. Understanding the role of aqueous reactions in the maturation of organic matter can be substantially improved by examining the reactivity of individual model compounds in laboratory experiments. We will present results from experimental studies on the hydrothermal reactivity of monocyclic aromatic compounds (MAC; benzene, toluene, phenol, cresols, etc.). These compounds are particularly suitable for such studies because MAC have relatively high aqueous solubilities and represent a significant fraction of the organic matter found in geologic environments.

EXPERIMENTAL

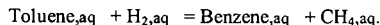
The experiments were conducted in a flexible-cell hydrothermal apparatus (3) using a gold reaction cell with titanium fittings. The reaction cell was equipped with a valve that allowed subsamples to be taken during the course of the experiment, so that the progress of the reactions could be followed over time. Experiments were carried out at either 300° or 330°C and 350 bars. Aqueous solutions of the compound to be studied were either loaded in the cell before heating or injected through the valve after an equilibration period. Assemblages of iron oxide and sulfide minerals were also included within the reaction cell. The intent of including these minerals is two-fold: first, to buffer the oxidation state of the system, and, second, to provide potential catalytic surfaces similar to those typically found in geologic environments. Mineral assemblages used in the experiments included pyrite-pyrrhotite-magnetite (PPM), hematite-magnetite-pyrite (HMP) and hematite-magnetite (HM).

RESULTS AND DISCUSSION

The principal reaction products from heating aqueous solutions of toluene were benzene and CO₂ (Figure 1). Other identified reaction products included phenol, benzoic acid, and cresols. Trace amounts of methane and other hydrocarbons were also observed, but these compounds appeared to derive from small amounts of organic matter in the minerals and not from toluene. Benzene and CO₂ were produced in a one-to-one ratio, suggesting that the formation of benzene from toluene proceeded by an oxidative decarboxylation reaction pathway:



rather than by demethylation:

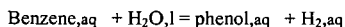


Benzoic acid appears to be an intermediate product of this reaction.

Aqueous solutions of benzoic acid decomposed rapidly during heating to benzene and CO₂ (plus minor phenol and toluene; Figure 2). Production of benzene from benzoic acid was much more rapid than the production from toluene, indicating that the formation of benzoic acid is the rate-limiting step in the reaction pathway from toluene to benzene.

None of the experiments conducted to date have shown any evidence for the decomposition of the aromatic ring from MAC. In all cases, the aromatic moiety from the original compound can be accounted for among the reaction products and remaining reactant. Thus, it appears that the aromatic ring is highly persistent under hydrothermal conditions, and reactions are limited to transformations among MAC with different substituent groups on the aromatic ring.

Comparisons of the relative concentrations of reaction products with predicted equilibrium ratios based on the thermodynamic properties of individual compounds indicates that reactions among several MAC compounds may rapidly approach equilibrium. For instance, equilibrium ratios of benzene to phenol predicted for the reaction



agree closely with the measured ratios in the experiments (Figure 3), suggesting that this reaction equilibrates very rapidly at the experimental temperatures. Consequently, it appears that the relative concentrations of benzene and phenol were controlled by chemical equilibrium between the compounds as the experiments progressed (note that this is strictly a *metastable* equilibrium, since both compounds should decompose almost completely to a mixture of CO_2 and methane as stable thermodynamic equilibrium of the system is approached). The possibility that other pairs of MAC compounds (e.g. toluene/cresols, toluene/benzene) may also reach equilibrium proportions is being investigated in ongoing experiments.

CONCLUSIONS

The experimental results demonstrate that monocyclic aromatic compounds readily undergo reactions in aqueous solutions at elevated temperatures, and indicate that these reactions mostly involve transformations among MAC with different substituent groups. The reactivity of MAC implies that similar reactions may play a large role in controlling the relative proportions of these compounds in geologic environments such as petroleum reservoirs and hydrothermal systems. Furthermore, the results suggest that the relative proportions of benzene and phenol (and perhaps other MAC) may be controlled by metastable equilibrium reactions taking place in the aqueous phase and involving water as a reactant. Since these reactions involve oxidation/reduction, the relative amounts of benzene and phenol in geologic environments should reflect the oxidation state of the system.

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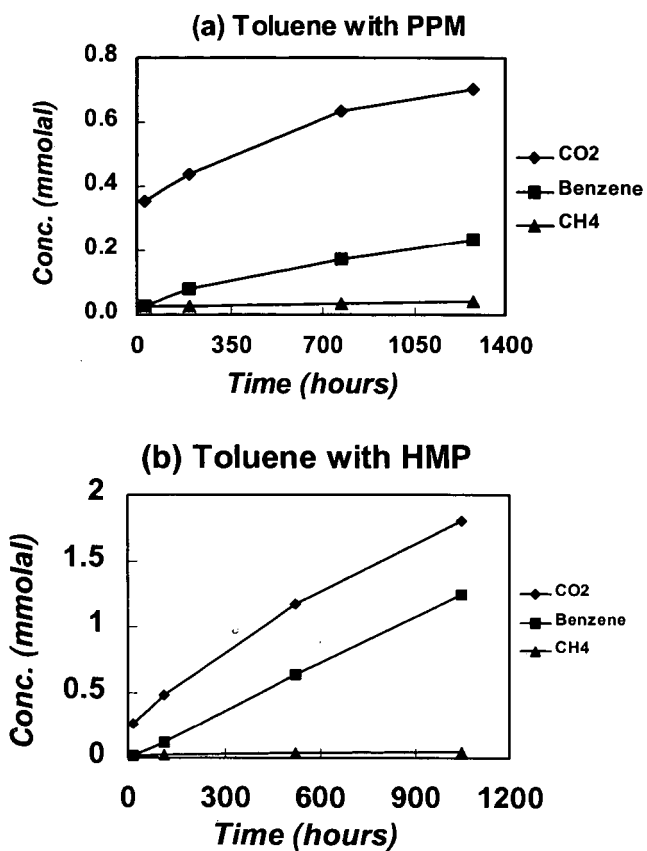


Figure 1. Selected reaction products from heating aqueous solutions of toluene at 330°C in the presence of the mineral assemblages (a) PPM and (b) HMP.

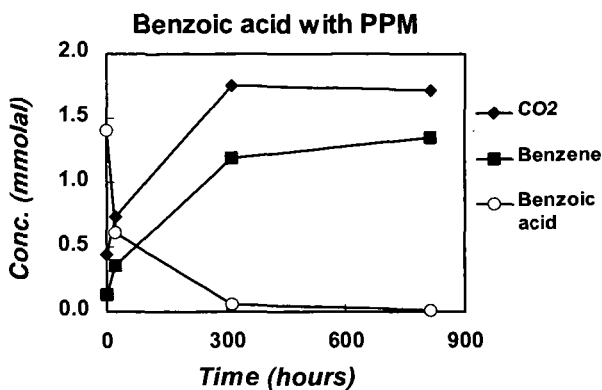


Figure 2. Selected reaction products from heating an aqueous solution of benzoic acid at 330°C in the presence of the mineral assemblage PPM.

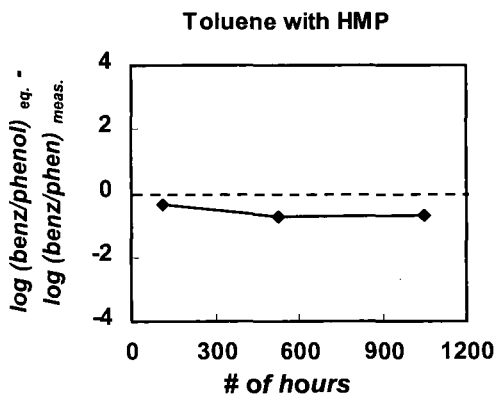


Figure 3. Difference between the predicted equilibrium ratio for benzene to phenol and the measured ratio for reaction products following heating of an aqueous solution of toluene at 330°C in the presence of the mineral assemblage HMP. Note that ratios are given on a log scale. Equilibrium ratios calculated using SUPCRT (4) with thermodynamic data from references 5,6 and 7.